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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) **Process for the Production of Rubber Vulcanizates Having  
Reduced Hysteresis Losses and Moldings of These  
Vulcanizates**

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A PROCESS FOR THE PRODUCTION OF RUBBER VULCANIZATES  
HAVING REDUCED HYSTERESIS LOSSES AND MOLDINGS OF THESE  
VULCANIZATES

A B S T R A C T

Carbon-black-filled rubber vulcanizates having reduced hysteresis losses may be obtained by mixing unvulcanized rubber with carbon black in the presence of certain sulfides at elevated temperature and vulcanizing the resulting mixture.

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A PROCESS FOR THE PRODUCTION OF RUBBER VULCANIZATES  
HAVING REDUCED HYSTERESIS LOSSES AND MOLDINGS OF THESE  
VULCANIZATES

5 This invention relates to a process for the production of carbon-black-filled rubber vulcanizates having reduced hysteresis losses by shearing of carbon-black-filled rubber in the presence of certain disulfides. The invention also relates to moldings of vulcanizates produced by this process, including for example vehicle tires, conveyor belts, drive belts and compressed-air bellows.

10 In rubber technology, a hysteresis loss is understood to be the energy loss which is irreversibly converted into heat in the event of dynamic stressing of the elastomer. The measured quantity for hysteresis losses is the  $\tan \delta$  which is defined as the ratio of loss modulus to storage modulus, cf. for example DIN 53 513 and DIN 53 535. Any reduction in the  $\tan \delta$  in the applicationally important temperature/frequency or amplitude range leads, for example, to reduced heat buildup in elastomers. Tires of rubber having a reduced hysteresis loss are distinguished by reduced rolling resistance and, hence, by lower fuel consumption of the vehicles fitted with them.

20 US-PS 4,690,965 describes, for example, carbon-black-filled rubber vulcanizates which show reduced heat buildup and, hence, a reduced hysteresis loss by virtue of their content of nitrosoanilines. However, on account of the danger of carcinogenic nitrosamines being formed trans-nitrosation, there is a need for rubber auxiliaries which are free from nitroso groups.

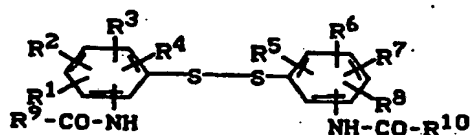
30 It has now surprisingly been found that carbon-black-filled rubber vulcanizates having reduced hysteresis losses can be obtained by mixing unvulcanized rubber with carbon black in the presence of di(acylaminoaryl) disulfide free from nitroso groups at elevated temperature and vulcanizing

the resulting mixture in known manner. The principal advantage of the process according to the invention is that the disulfides used to improve hysteresis do not affect the mechanical properties of the vulcanizates, such as for example their strength, elongation and modulus, to the extent where the vulcanizates no longer satisfy the demands made of the end products (for example tires or drive belts).

The use of di(o-acylaminoaryl) disulfides as masticating agents for natural and synthetic rubber is known (US-PS 2,470,948). It is known that rubbers are masticated to reduce viscosity. Accordingly, the auxiliaries according to US-PS 2,470,948, as normal for masticating agents, are mixed with the rubber before addition of the usual fillers and auxiliaries, particularly before the addition of carbon black (for example on mixing rolls or in an internal mixer at 120°C), and the resulting mixture is then sheared until the desired viscosity is reached. The reduced viscosity established in this way enables fillers and auxiliaries to be incorporated without difficulty; a homogeneous mixture could otherwise only be obtained with difficulty. The shearing of carbon black/rubber mixtures in the presence of di(o-acylaminoaryl) disulfides is neither disclosed nor suggested in US-PS 2,470,948.

The present invention relates to a process for the production of carbon-black-filled rubber vulcanizates by mixing of unvulcanized rubber, carbon black and, optionally, other auxiliaries and subsequent vulcanization, comprising adding

- (i) to the unvulcanized rubber,
- (ii) 10 to 120% by weight and preferably 30 to 80% by weight, based on rubber (i), carbon black and
- (iii) 0.1 to 10% by weight and preferably 0.1 to 3% by weight, based on rubber (i), diphenyl sulfide corresponding to the following formula



in which

$R^1$  to  $R^8$  independently of one another represent hydrogen, fluorine, chlorine, bromine,  $C_{1-8}$  and preferably  $C_{1-4}$  alkyl, more especially methyl,  $C_{1-8}$  and preferably  $C_{1-4}$  alkoxy, more especially methoxy, nitro and

$R^9$  and  $R^{10}$  independently of one another represent hydrogen,  $C_{1-18}$ , preferably  $C_{1-12}$  and more preferably  $C_{1-3}$  alkyl,  $C_{2-18}$ , preferably  $C_{2-12}$  and more preferably  $C_{2-4}$  alkenyl,  $C_{3-12}$  cycloalkyl and alkenyl,  $C_{3-12}$  aryl,

the above-hydrocarbon radicals for  $R^9$  and  $R^{10}$  optionally being substituted by halogen (fluorine, chlorine), carboxyl, hydroxy, nitro, amino, di- $C_{1-3}$ -alkylamino, mercapto,  $C_{1-3}$  alkoxy and nitro,

at melt temperatures of at least  $140^\circ\text{C}$  and preferably of at least  $150^\circ\text{C}$  and at shear rates of 1 to  $1000\text{ sec}^{-1}$  in such a way that at least 10% by weight carbon black (ii), based on rubber (i), are added before there is any significant reduction in the molecular weight of the rubber.

Rubbers (i) suitable for the process according to the invention include not only natural rubber, but also synthetic rubbers containing at least 5% by weight copolymerized units emanating from a  $C_{4-12}$  diene. Preferred synthetic rubbers are described, for example, in W. Hoffmann, Kautschuk-Technologie, Genter Verlag, Stuttgart 1980. They include *inter alia*

- BR - polybutadiene
- ABR - butadiene/C<sub>1-4</sub> alkylacrylate copolymers with acrylate contents of 5 to 60% by weight and preferably 15 to 50% by weight,
- 5 CR - polychloroprene
- IR - polyisoprene
- SBR - styrene/butadiene copolymers with styrene contents of 1 to 60% by weight and preferably 20 to 50% by weight,
- 10 NBR - butadiene/acrylonitrile copolymers with acrylonitrile contents of 5 to 60% by weight and preferably 10 to 50% by weight

and mixtures of these rubbers. The rubbers to be used for the process according to the invention have glass transition temperatures below 20°C and preferably below 0°C, as determined in the torsion pendulum test according to DIN 53 445.

Particularly preferred rubbers (i) are polybutadiene and styrene/butadiene copolymers. SBR solution and emulsion polymers are preferred for vehicle tires, particularly for treads. SBR solution polymers are particularly preferred. The content of 1,2-bonds may vary within wide limits and is generally between 5 and 80%, based on the number of copolymerized butadiene groups.

If desired, other rubbers (i) may be added to and mixed with individual rubbers (i) before vulcanization and before or after the addition of carbon black (ii) and disulfide (iii).

Any reinforcing carbon blacks may be used for the process according to the invention. Preferred surfaces are in the range from 35 to 200 m<sup>2</sup>/g (CTAB determination). SAF, HAF, FEF, ISAF and SRF carbon blacks are mentioned in particular. Mixtures of two or more different carbon blacks or mixtures of carbon blacks with silicas (with and without filler activators) may readily be used. The degree of

filling may be varied within wide limits, 30 to 80 parts by weight carbon black (ii), including silica if any, to 100 parts rubber (i) being preferred.

- 5 Preferred disulfides (iii) include, for example, those in which all the substituents  $R^1$  to  $R^8$  are hydrogen and in which the acylamino groups are in the 2,2', 3,3' or 4,4'-position, the substituents  $R^9$  and  $R^{10}$  independently of one another, but preferably together, assuming the following meanings:

-H



-CH<sub>3</sub>



-CH<sub>2</sub>CH<sub>3</sub>



-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>



-C<sub>17</sub>H<sub>35</sub>

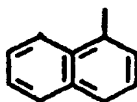
-CH<sub>2</sub>Cl



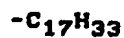
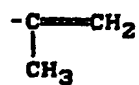
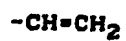
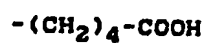
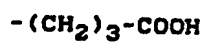
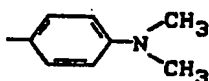
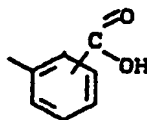
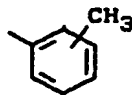
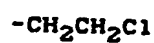
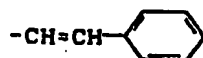
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-CCl<sub>3</sub>



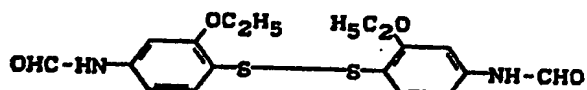
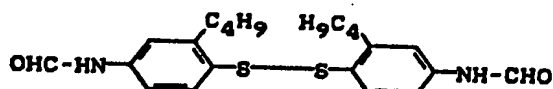
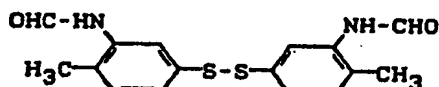
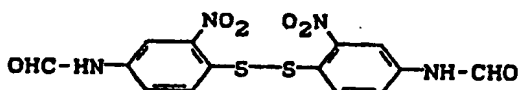
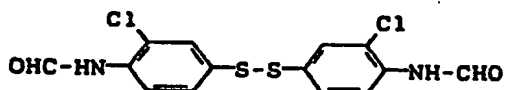
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Preferred sulfides (iii) also include, for example, compounds in which the substituents  $R^9$  and  $R^{10}$  are hydrogen and in which the phenylene radicals each bear a chlorine, nitro, methyl, butyl or ethoxy group.

The following are preferred examples of such compounds:



The disulfides (iii) are known from the literature or may be produced by methods known *per se*, *cf.* for example US-PS 2,470,948; Farm., Ed. Sci. 29 (1974) 2, 120-128.

A particularly suitable method is the acylation of diaminodiphenyl disulfides which in turn may largely be produced by three different methods, namely:

- a) by hydrolysis of benzthiazoles and oxidation to the disulfide, *cf.* Beilstein, Vol. 13 E III, 907;
- b) by nucleophilic substitution of aromatic nitro com-

pounds by sodium hydrogen sulfide with simultaneous reduction of the nitro group to the amino group, followed by oxidation of the mercaptan to the disulfide; cf. Methoden der Organischen Chemie (Houben-Weyl), Vol. 11/1, Georg-Thieme-Verlag, Stuttgart 1957, page 416 and

- c) by reduction of nitroaryl sulfochlorides to amino-thiophenols, followed by oxidation to the disulfide, cf. Methoden der Organischen Chemie (Houben-Weyl), Vol. 11/1, Georg-Thieme-Verlag, Stuttgart 1957, page 431.

The disulfides (iii) used will generally be those of which the half life period in the rubber mixture used at the processing temperature (melt temperature) is less than half the processing time, i.e. disulfides (iii) which have a half life period of less than 3 minutes. Particularly preferred disulfides (iii) are those of which the half life period is between one tenth and one third of the processing time.

For the process according to the invention, standard fillers and auxiliaries such as, for example, plasticizers, resins, factices and stabilizers may be added to the rubber mixtures to obtain certain crude mixture or vulcanization properties.

The melt temperature of the mixture required for the process according to the invention of preferably 140 to 250°C and more preferably 150 to 200°C may be obtained by external application of heat or by corresponding friction during the mixing process. The desired melt temperature is generally below the decomposition temperature of the rubber (i) used. In special cases, i.e. where the mixture has an extremely short residence time in the high temperature zone, the decomposition temperature of the rubber (i) may even be exceeded providing no significant decomposition occurs (on account of the short residence time). In most

cases, it may be advisable to base the choice of the melt temperature on the half life period of the disulfide (iii) used at that temperature.

5 Preferred mixing units are the mixing rolls, internal mixers and mixing extruders typically used in the rubber industry which generally operate with shear rates of 1 to 1000 sec.<sup>-1</sup> and preferably 1 to 200 sec.<sup>-1</sup>.

10 The mixing times are governed by the desired degree of dispersion of the carbon black (ii) and the remaining mixture constituents in the mixture. They are often between 30 and 1000 seconds and are preferably between 30 and 360 seconds. Where internal mixers are used, excellent results are obtained with mixing times of this order.

15 In the context of the invention, a "significant reduction" in the molecular weight of the rubber would be a reduction of more than 10% and preferably more than 5% in the weight average molecular weight  $\bar{M}_w$ .

20 The carbon black (ii) is preferably added before a melt temperature of 140°C and preferably 150°C is reached. The disulfides (iii) may be added to the rubber (i) together with the total quantity of carbon black (ii) or with parts thereof, in which case the remaining quantity of carbon black is subsequently added in accordance with the formulation.

25 The crosslinking systems known from rubber technology, such as sulfur, peroxides, polyisocyanates, metal oxides, phenolic resins and combinations thereof, may be used for vulcanization. The crosslinking system used for vulcanization will preferably be adapted to the type of rubbers (i) used. Sulfur crosslinking systems are particularly preferred.

30 The crosslinking systems are preferably added at temperatures below 130°C and preferably at temperatures below 100°C. Vulcanization may take place at temperatures in the range from 100 to 200°C and preferably at temper-

atures in the range from 130 to 180°C, optionally under a pressure of 10 to 200 bar.

Articles subjected to severe dynamic stressing, such as vehicle tires, conveyor belts, drive belts, such as V belts and gear belts, compressed-air bellows, etc., may be produced by the process according to the invention. Accordingly, the present invention relates to moldings of vulcanizates obtainable by the process according to the invention.

In the following Examples, parts are parts by weight.

#### EXAMPLES

The following compositions were prepared in accordance with the following mixing sequence in a laboratory compounder (of the type manufactured by Haake Mess-Technik GmbH & Co., Karlsruhe 41) at various shell temperatures of the mixing compartment and at rotational speeds of the CAM blades of 30 to 100 r.p.m.:

After  
[mins.]

	addition of rubber
0.5	addition of half the carbon black together with the disulfide
1.5	addition of the other half of the carbon black and the remaining components
4-6	ejection

The final batch temperature is shown in the Tables. The vulcanization system was subsequently incorporated in the mixture on laboratory mixing rolls at 40 to 60°C.

#### Formulation:

137.5 parts	*Buna SL 750 (a product of Bunawerke Hüls GmbH, Marl) containing 100 parts solution SBR and 37.5 parts oil
70 parts	carbon black N 220 (a product of Degussa, Wesseling)

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1 part stearic acid  
3 parts zinc oxide  
1 part Vulkanox 4010 NA (a product of  
BAYER AG, Leverkusen = IPPD = N-isopropyl-N'-phenyl-p-  
phenylenediamine  
1 part disulfide of formula I

1.8 parts sulfur

1.2 parts Vulkacit NZ (a product of BAYER AG,  
Leverkusen) = TBBS = benzthiazyl-2-tert.-  
butyl sulfenamide

Vulcanization took place for 20 minutes at 150°C.

EXAMPLES 1-3 and COMPARISON EXAMPLE 1

These Examples demonstrate the effect of the final  
batch temperature with reference by way of example to 2,2'-  
diformamidodiphenyl disulfide ( $R^1-R^{10} = H$ ). Comparison  
Example C-1 contains no hysteresis promoter.  $\Delta \tan \delta$   
represents the percentage change in the  $\tan \delta$  in relation  
to the disulfide-free standard.

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Example	1	2	3	C-1
Shell temperature	120°C	150°C	170°C	120°/150°/170°C
Batch temperature	152°C	176°C	197°C	152°/176°/191°C
Strength [MPa]	20.5	23.5	20.6	23.0/23.3/18.8
Elongation at break [%]	511	560	426	592/579/525
Modulus 100* [MPa]	2.1	2.1	2.7	1.9/2.1/1.9
Modulus 300* [MPa]	10.0	10.5	13.6	9.0/10.3/9.1
tan δ 50°C	0.33	0.33	0.32	0.33/0.33/0.34
tan δ 90°C	0.30	0.29	0.27	0.31/0.31/0.31
Δ tan δ 90°C [%]	-3.3	-6.5	-13	-
tan δ 110°C	0.27	0.29	0.23	0.28/0.28/0.28
Δ tan δ 110°C [%]	-3.6	-10.8	-18	-

\* The "modulus 100" value is the stress at 100% elongation; similarly, the "modulus 300" value is the stress at 300% elongation.

COMPARISON EXAMPLES 2-4

In these Comparison Examples, the effect of the mixing sequence is demonstrated by comparison with Example 3. Once again, the addition was 2,2'-diformamidodiphenyl disulfide.

In Comparison C-2, the disulfide was subsequently added to the mixture together with the vulcanization system. Tensile strength deteriorated considerably as a result.

Buna SL 750 was first mixed with the disulfide to be used in accordance with the invention (as in conventional mastication) for 5 minutes at a shell temperature of 120°C (melt temperature 150°C) in comparison C-3 and for 5 minutes at a shell temperature of 170°C (final melt temperature 190°C) in comparison C-4, the basic mixture was prepared in a second mixing step and the vulcanization system subsequently added on mixing rolls. There was no clear reduction in the hysteresis losses.

Example	3	C-2	C-3	C-4
Shell temperature for basic mixture	170°C	120°C	120°C	120°C
Final batch temperature	198°C	154°C	153°C	150°C
Strength [MPa]	20.6	12.9	20.9	17.8
Elongation at break [%]	426	353	518	450
Modulus 100 [MPa]	2.7	2.1	2.1	1.8
Modulus 300 [MPa]	13.6	10.3	10.4	10.0
$\Delta \tan \delta$ 30°C [%]	-3	n.d.	-1	-3
$\Delta \tan \delta$ 70°C [%]	-11	n.d.	+1	-3
$\Delta \tan \delta$ 110°C [%]	-18	n.d.	-3	-4

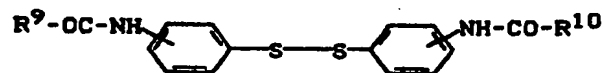
n.d. = not determined





EXAMPLES 4-9

These Examples demonstrate the influence of the position of the acylamino group and of the substituents  $R^9$  and  $R^{10}$  on the effect of the process according to the invention.

5



Example	R <sup>9</sup> , R <sup>10</sup>	Position of acylamino group	Strength [MPa]	Modulus 300 [MPa]	$\Delta \tan \delta$ 100°C [%]
4	-CH <sub>3</sub>	2,2'	20.0	11.9	-16
5	-CH <sub>3</sub> -CH <sub>3</sub>	2,2'	21.6	10.9	-13
6	-CH=CH <sub>2</sub>	2,2'	20.6	11.9	-13
7		2,2'	21.6	11.2	-11
8	-H	4,4'	21.1	10.7	-8
9		4,4'	22.0	11.7	-12

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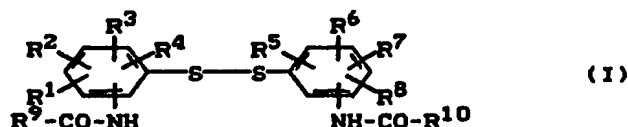
**CLAIMS**

1. A process for the production of carbon-black-filled rubber vulcanizates by mixing of unvulcanized rubber, carbon black and, optionally, other auxiliaries and subsequent vulcanization, comprising adding

(i) to the unvulcanized rubber,

(ii) 10 to 120% by weight, based on rubber (i), carbon black and

(iii) 0.1 to 10% by weight, based on rubber (i), diphenyl sulfide corresponding to the following formula



in which

R<sup>1</sup> to R<sup>8</sup> independently of one another represent hydrogen, fluorine, chlorine, bromine, C<sub>1-8</sub> alkyl, C<sub>1-8</sub> alkoxy, nitro and

R<sup>9</sup> and R<sup>10</sup> independently of one another represent hydrogen, C<sub>1-18</sub> alkyl, C<sub>2-18</sub> alkenyl, C<sub>3-12</sub> cycloalkyl and alkenyl, C<sub>3-12</sub> aryl,

at melt temperatures of at least 140°C and at shear rates of 1 to 1000 sec<sup>-1</sup> in such a way that at least 10% by weight carbon black (ii), based on rubber (i), are added before there is any significant reduction in the molecular weight of the rubber.

2. A process as claimed in claim 1, in which 30 to 80% by weight carbon black, based on rubber (i), is used.

3. A process as claimed in claims 1 and 2, in which 0.1 to 3% by weight diphenyl sulfide (iii), based on rubber (i) is used.

4. A process as claimed in claims 1 to 3, in which the

substituents  $R^1$  to  $R^8$  are selected from the group consisting of hydrogen, chlorine and nitro in such a way that at least six of these substituents are hydrogen and the substitution at both phenylene rings is symmetrical.

- 5      5. A process as claimed in claims 1 to 4, in which the substituents  $R^9$  and  $R^{10}$  are hydrogen, methyl or ethyl.
6. A process as claimed in claims 1 to 5, in which the acylamino groups of the disulfide (iii) are in the opposition to the sulfur.
- 10     7. A process as claimed in claims 1 to 6, in which the melt temperature during mixing is 150 to 200°C.
8. A process as claimed in claims 1 to 7, in which vulcanization is carried out at temperatures of 100 to 200°C.
- 15     9. Moldings of vulcanizates obtainable by the process claimed in claims 1 to 8.

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Patent Agents

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